SYNTHESIS AND CHARACTERIZATION OF La DOPED $Bi_4Ti_3O_{12}$ CERAMICS

By

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Thesis submitted
in partial fulfilment for the Degree of
MASTER OF SCIENCE IN PHYSICS

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Dedicated to all
My well wishers

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Certificate from the Supervisor

This is to certify that the thesis entitled, "***Synthesis and characterization of La doped $Bi_4Ti_3O_{12}$ ceramics***" prepared by **Ms. Luna Bhowmick ,** Roll No: 410PH2121, Of Department of Physics of **National Institute of Technology, Rourkela**, for the partial fulfilment of the requirements for the degree of **MASTER OF SCIENCE IN PHYSICS, at NIT, Rourkela,** is absolutely based upon the research work carried out by her under my supervision and guidance.

To the best of my knowledge, these results have not been submitted by her for the award of any other degree or diploma.

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DECLARATION

I certify that

1. The work contained in this thesis is an original record of the work carried out by me under the supervision of my supervisor.

2. The work has not been submitted to any other Institute for any degree or diploma.

3. I have abided by the norms and guidelines given in the Ethical Code of Conduct of the Institute.

4. Wherever I have used materials (data, theoretical analysis, and text) from other sources, I have given them due credit by mentioning them at the end of the borrowed material of the thesis and have given their complete details in the references.

Signature of the Student

ACKNOWLEDGEMENT

My deepest regards to my guide and supervisor, Dr. Pawan Kumar. Without his kind guidance, I would not have completed my annual project successfully. I also wish to thank all the Phd scholars at Electroceramic Laboratory, Dept. of Physics, National Institute of Technology, Rourkela for extending a helping hand and enlightening me with knowledge during the course of my project work. A special mention, however, has to be made of Sridevi Swain who supervised over my work from the very beginning till the end, and helping with her kind guidance and support whenever i needed her help. Last, but not the least, my sincere thanks goes to Senthil Venkatesan who helped me in every possible way to learn and gain knowledge in the field of electroceramics.

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ABSTRACT

$Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) was prepared by the conventional solid state route as well as the chemical route. Calcination of the sample prepared through the solid state route was done at 750^0C for 4 hours and of the sample prepared through the chemical route at 600^0C for 4 hours. XRD of the samples was done in which BLT layered perovskite phase was confirmed. The samples were sintered using the conventional sintering method at 1150^0C for 4 hours and that of the sample prepared by chemical route was done at 1150^0C for 2 hours. Density measurement was done to confirm final densification after sintering. SEM images of the samples were taken which showed dense microstructure and uniform grain size. Comparative study of dielectric properties of the samples prepared by both solid state and chemical route were performed. PE loop measurements were done to confirm the ferroelectric nature of the sample.

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Chapter 1: Introduction

The world of electroceramics is advancing fast as the need of the generation rises even faster with the invention of new technological devices each day. The development of this field depends entirely on the effort put in to it to obtain desirable properties for applications in newer technologies and the cut throat competitions is already successful in giving researchers the impetus to go about the development of the field of electroceramics. An electroceramic material possesses different important properties for suitability of use in electronic equipments and gadgets. These ceramics however have to have exceptional properties as compared to the presently used ceramics to be able to take their place because of some or the other limitations of the presently used ceramic materials. Few properties of electroceramics has been explained below in brief.

1.1 Dielectric Properties of Solids

Dielectric materials are kind of insulating materials which normally do not contain any free charge carriers for conduction of electricity. However, on application of an external electric field the centres of the positive and negative charges get displaced from their coinciding positions and thus giving rise to some amount of dipole moment which in turn leads to charge conduction.

1.1.1 Polarization and Susceptibility

When a dielectric is placed in an external electric field, the positive and negative charges are displaced from their equilibrium positions by very small distances(less than an atomic diameter) throughout the volume of the dielectric. This results in the formation of a large number of dipoles each having some dipole moment in the direction of the field. The material is said to be polarized with a polarization **P** defined as the dipole moment per unit volume. The externally applied electric field is called **Polarization Field[1]**.

$$P = \varepsilon_O \chi_e E$$

Where ε_O is the permittivity of free space and χ_e is the electric susceptibility.

1.1.2 Dielectric Constant

Though formulas containing displacement vector, polarization and local field are often used to measure the dielectric constant of a material but in this context we use the following formula for the calculation of dielectric constant of a material.

$$\varepsilon_r = \frac{C \times d}{\varepsilon_o \times A}$$

Where ε_r is called the relative permittivity or dielectric constant of a material, C is the capacitance, d is the thickness and A is the area of the sample. The simplest definition of dielectric constant is

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_o}$$

Where ε is the permittivity of the dielectric medium.

1.1.3 Types of Polarization:

1) Electronic polarization
2) Ionic polarization
3) Dipolar polarization
4) Space charge polarization

1.1.3.1 Electronic Polarization: Electronic polarization occurs in a material due to the displacement of the electron cloud of an atom relative to its nucleus in the presence of an externally applied electric field. The polarization as well as the dielectric constant of a material at optical frequencies result mainly from the electronic polarization of materials.

1.1.3.2 Ionic Polarization: The ionic polarization arises due to displacement of a charged ion relative to other ions in a solid. The ionic contribution is important at low frequencies.

1.1.3.3 Dipolar Polarization: A molecule, such as H_2O, having a permanent dipole moment is called a dipolar or polar molecule and a substance containing such molecules is called a dipolar substance. The dipolar polarization is the property of dipolar substances. In the absence of an external electric field, the dipoles have random orientations and therefore there is no net polarization. However, in the presence of an applied field, the dipoles orient themselves along the field and produce orientational or dipolar polarization. The thermal agitation of the molecules tends to counteract the ordering effect of the electric field and an equilibrium state is reached wherein the different dipoles make all possible angles varying from zero to π radians with the field direction.

1.1.3.4 Space Charge Polarization: This kind of polarization arises due to surface accumulation of charges at the interface or at the grain boundary of a polycrystalline material. The ions diffuse over appreciable distances in response to the applied field giving rise to redistribution of charges in the dielectric medium.

Total Polarizability: This is the sum of the four different types of polarizations.

1.1.4 Frequency Dependence of Dielectrics

Dielectric constant ε_r is inversely proportional to frequency. The dielectric loss at low frequencies is mainly due to d.c resistivity but at high frequencies, dielectric loss occurs mainly because of dipolar rotations and ionic transitions from the lower energy states to higher energy states. Because of the upward transition, the energy is absorbed from the applied field. The absorption of energy is possible if dipolar polarization or permanent dipole moment exists. The plot of frequency dependence of dielectrics is accounted for in figure 1.

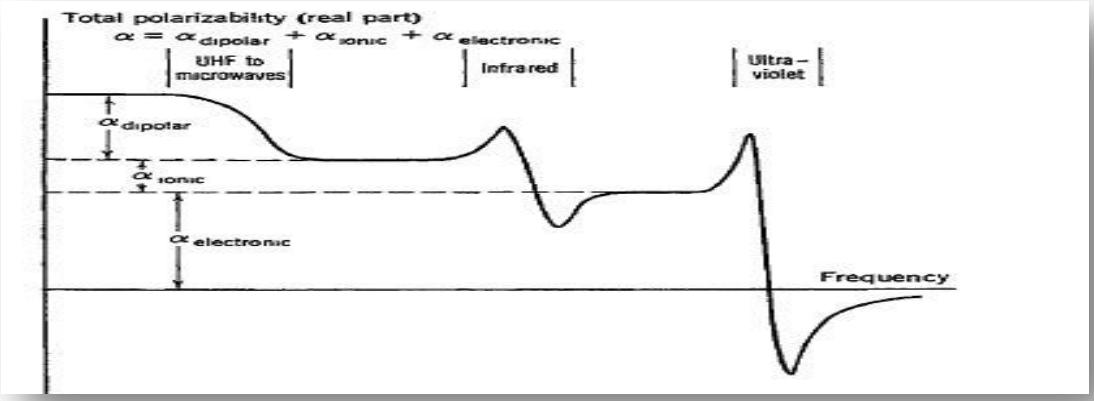


Fig1: Frequency dependence of various contributions to polarization[1]

1.1.5 Dielectric Relaxation

For polarization to attain its maximum value, dielectrics take some time. This is so because of the forces between adjacent molecules which prevent the alignment of the dipoles along the externally applied electric field direction. This phenomenon is termed as dielectric relaxation. It is a characteristic property of relaxor ferroelectrics and is not exhibited by all dielectrics.

1.1.6 Ferroelectric Behaviour

Ferroelectricity was first discovered in Rochelle salt. Ferroelectric behaviour of a material is its property to retain some amount of polarization on removal of an externally applied electric field. Polarization versus electric field curve for a ferroelectric material shows a loop termed as hysteresis loop.

1.1.7 Dielectric Loss

Ferroelectric materials are very often dielectrics. For most applications of ferroelectric materials the dielectric constant and dielectric loss are important practical parameters, and studies of the dielectric properties provide great deal of information for understanding the molecular structure and the mechanism of electric polarization in ferroelectric materials.

Suppose a parallel plate condenser is filled with a dielectric material. When an alternative electromotive force δ with frequency ω is applied on this condenser, an alternating current i flows through the condenser,

$$i = j\,\omega\,\varepsilon_r C_O \delta \quad (j=\sqrt{-1})$$

where C_O is the capacity of the parallel plate condenser without any medium (i.e. in vacuum) and ε_r, the relative dielectric constant is a function of ω. Because the dielectric loss (including the leakage current exists in dielectric materials ε_r must be written as a complex number:

$$\varepsilon_r^*(\omega) = \varepsilon'(\omega) - j\,\varepsilon''(\omega)$$

Where $\varepsilon'(\omega)$ is the real part of the dielectric constant and $\varepsilon''(\omega)$ is the imaginary part. The latter represents the dielectric loss. Instead of ε'', $\tan\delta$ (tangent of the dielectric loss angle) is most frequently used to express this loss and its definition is

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'}$$

1.2 Properties of Ferroelectric Materials

1.2.1 Crystal Symmetry

A crystal can be grouped under 230 space groups and 32 point groups in three dimensions. The 32 point groups can be further classified as centrosymmetric and non-centrosymmetric. All non-centrosymmetric point groups show piezoelectric effect under unique directional axes.

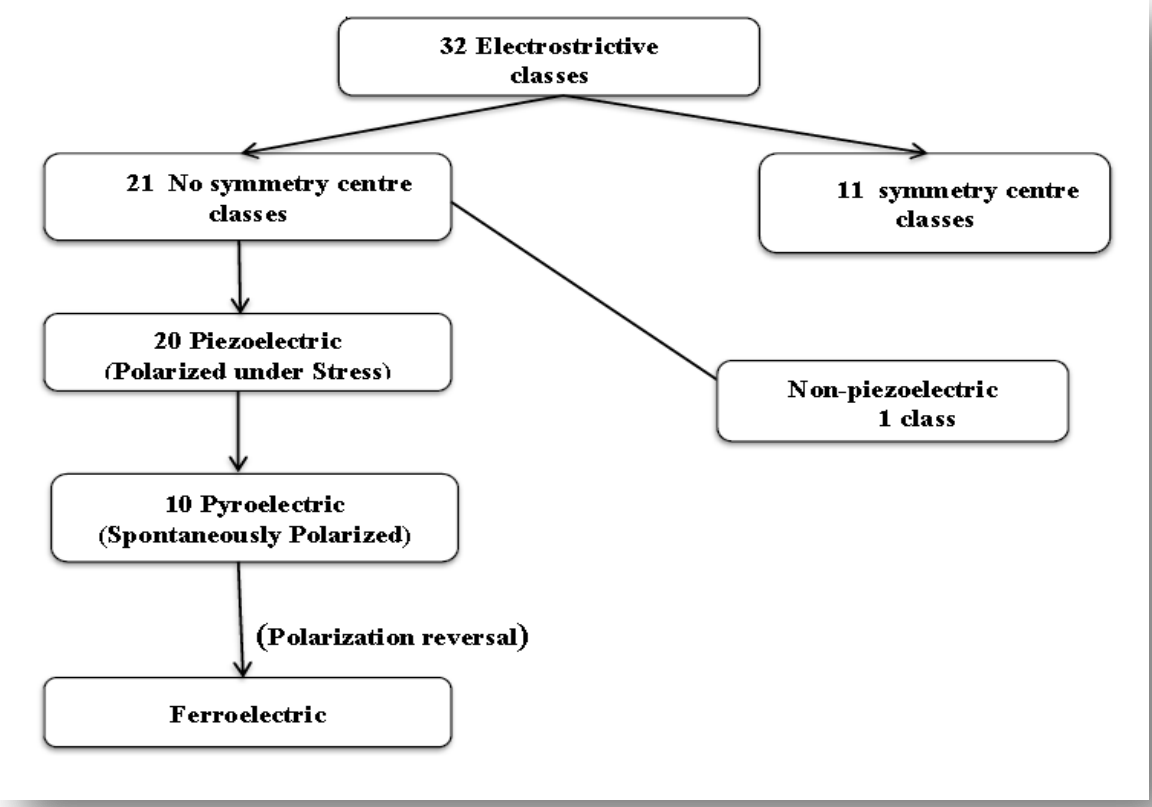


Fig 2: Interrelationship of piezoelectric and subgroups on the basis of symmetry

NOTE: Out of 20 point groups which show piezoelectric effect, 10 point groups (including 1, 1m, 2, 2mm, 3, 3m, 4, 4mm, 6, 6mm) have only one unique direction axis. Such crystals are called polar crystals as they show spontaneous polarization (i.e., polarization in the absence of an electric field)

1.2.2 Piezoelectricity and Converse Piezoelectricity

Derived from the greek word 'piezo' meaning 'to press tight', piezoelectricity is produced by the application of some amount of pressure on some materials like quartz which leads to development of charges on the surface giving rise to a potential difference which is proportional to the stress. Technically, piezoelectricity is the ability of certain crystalline materials to develop an electric charge proportional to a mechanical stress.

Converse piezoelectricity is defined as the production of a geometric strain on the application of an external voltage. Mathematically we may express both the piezoelectric and the converse piezoelectric
Effect in the form of a tensor notation as follows:

$$P_i = d_{ijk}\delta_{jk} \quad \text{(direct effect)}$$

$$\varepsilon_{ij} = d_{kij}E_k \quad \text{(converse effect)}$$

P_i is the polarization generated along the I-axis with respect to the applied stress.
δ_{jk} is the applied stress.
d_{ijk} is the piezoelectric coefficient.
ε_{ij} is the strain generated on applied field.
E_k is the applied field.

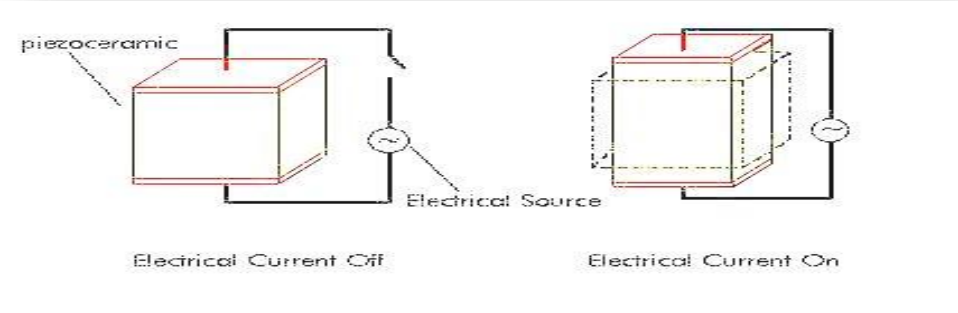


Fig3:Piezoelectric effect

1.2.3 Pyroelectric Effect

A crystal with polar axes shows piezoelectric effect but it is not necessary for it to possess a spontaneous polarization vector. This may be due to cancellation of dipole moments along the various polar axes which may in turn lead to a zero net polarization. Only crystals with unique polar axis (10 out of 21 non-centrosymmetric point groups) show a spontaneous polarization vector P_S along this axis. The value of this P_S depends on temperature. This effect is termed as pyroelectric effect and was first discovered in tourmaline crystal. The pyroelectric effect can be described in terms of the pyroelectric coefficient π. Gradual change in the temperature leads to a change in P_S. Mathematically,

$$\Delta P_S = \pi \Delta T$$

1.2.4 Hysteresis Loop

The magnitude and direction of the spontaneous polarization vector P_S can be reversed by applying an external electric field. This results in ferroelectric behaviour. Therefore all ferroelectrics are pyroelectrics but the converse need not be true (example: tourmaline crystal shows pyroelectricity but it is not ferroelectric).

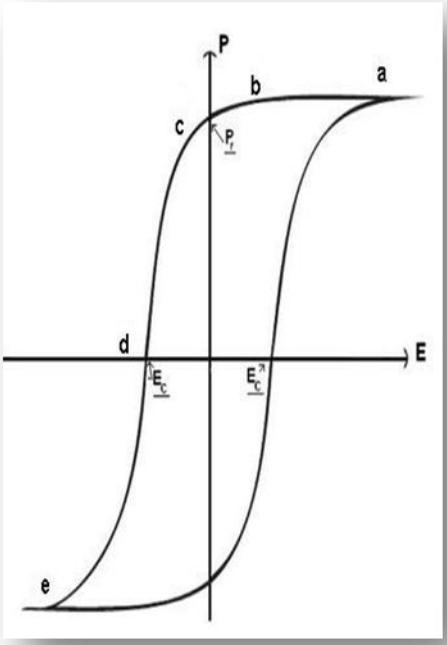


Fig4: Hysteresis loop

1.2.5 Ferroelectric domains

Domains are regions of uniform polarization within a ferroelectric crystal. Within a domain all the dipoles are aligned in the same direction. They are separated by one another by interfaces called ‘domain walls’. To obtain a single domain, electric field is sufficient. It causes motion of the domain walls. A very strong field may lead to polarization reversal. This is known as ‘domain switching’. The direction of spontaneous polarization can be reversed in ferroelectric materials. This is where we can differentiate between ferroelectrics and pyroelectrics. This can be best

understood from the polarization versus electric field hysteresis loop. As the electric field is increased the domains tend to align in the direction of the applied electric field. This considerably increases the polarization. At some critical value of the field, the polarization reaches a saturation value (P_{SAT}). But, on removal of the external field, surprisingly, the polarization does not drop down to zero. At zero applied field some of the domains remain aligned in the positive field direction. This is why the crystal shows remnant polarization P_r. For complete depolarization a field should be applied in the negative direction. The amount of negative field required to bring down the polarization back to zero is termed as coercive field strength E_C. As we increase the field to a higher value in the negative direction, the direction of polarization flips and a hysteresis loop is formed. The value of the spontaneous polarization P_S is obtained by extrapolating the curve onto the polarization axis.

Chapter 2: Material Selection

2.1 Literature Review

In 1995 Warren et al [7] found out that the reduction of the switchable polarization in $BaTiO_3$ crystals via repeated polarization reversals (fatigue) is accompanied by the trapping of electronic charge and atomic scale distortions in the perovskite oxygen octahedron. The distortions are proposed to involve oxygen vacancies.In 2001 Ding et al [6] wrote in his paper that $Bi_4Ti_3O_{12}$, (BTO) a Bi-layered perovskite oxide, shows fatigue after repeated ferroelectric polarization reversals. On the other hand, $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) is fatigue free. From an extensive transmission electron microscopy study, it was found that there is a high density of antiphase boundaries (APBs) in BLT like in the fatigue-free $SrBi_2Ta_2O_9$ but not in BTO. It was proposed that the existence of APBs possibly plays a key role in the fatigue-free behavior of Bi-layered perovskite oxides.

Thus based on the above literature review the $Bi_{3.25}La_{0.75}Ti_3O_{12}$ composition of Bismuth Lanthanum Titanate ceramic was chosen for this particular project. $Bi_{3.25}La_{0.75}Ti_30_{12}$ possesses layered perovskite structure. These compounds possess some plate like crystal structure which results in high anisotropy in ferroelectric properties due to low poling efficiency[2].

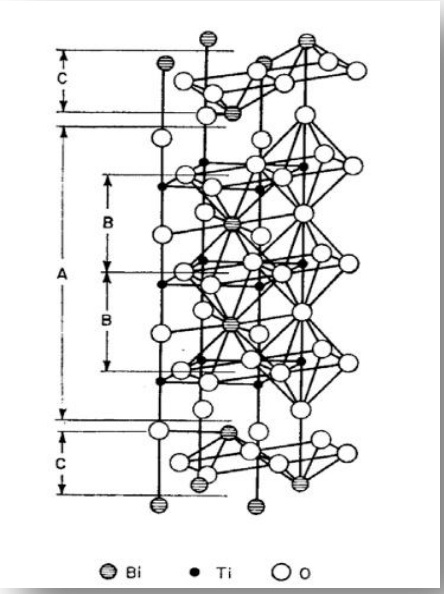


Fig5: Crystal structure of $Bi_4 Ti_3O_{12}$: C denotes $Bi_2 O_2^{2+}$ layers and B denotes units of hypothetical perovskite structure. and A denotes the perovskite multiple layer height.

2.2 Advantages of Layered Perovskite Structure

(i) High fatigue resistance

(ii) Low leakage current

(iii) Large mechanical quality factor (Q_m)

(iv) High transition temperature T_C

2.3 Disadvantages of Layered Perovskite Structure

(i) Low dielectric constant

(ii) Highly anisotropic

(iii) High coercive field(E_C)

(iv) Low remnant polarization(P_r)

2.4 Reasons for Selection of $Bi_{3.25}La_{0.75}Ti_3o_{12}$

$Bi_{3.25}La_{0.75}Ti_3O_{12}$,a bismuth layered structure ferroelectric(BLSF) ceramic is fatigue free which is highly desirable for memory applications and it has low leakage current which makes it safe for use in electronic equipments. High transition temperature ($T_{c)}$ enables use of BLT in high temperature applications.

Chapter 3: Optimization of Synthesis Process

Most of the properties of the samples depend on how the synthesis and characterization techniques are performed. Careful synthesis of the samples has to be done so that there is no chance of impurity creeping into it and careful control of the parameters such as temperature while calcining and sintering must be done so as to optimize the process and obtain best possible results.

The fatigue free material BLT was prepared by both the solid state route as well as the chemical route. The steps involved in the synthesis and characterization of the samples prepared by both these routes are stated below:

3.1 Solid State Route

This route of synthesis is best known for its cost effectiveness. The raw materials required for synthesis by this route are mainly solid chemicall precursors which are readily available and in most cases economical. This method of synthesis is quite easy and fast since rapid reactions take place between solid particles of the chemical precursors.

3.1.1 Raw Materials used

Optimum care should be taken while selecting raw materials for the sample to be prepared. The raw materials should be highly pure and the particle size of the powders should be in the sub-micron range for the solid phase reactions to take place by atomic diffusion.

Generally, the raw materials selected in this process are oxides (or, carbonates),so, this process is also known as the *oxide mixing technique*. The raw materials selected for the preparation of BLT were
Bismuth Oxide (Bi_2O_3), Lanthanum Acetate ($C_6H_9LaO_6$) and Titanium Dioxide (TiO_2).

3.1.2 Stoichiometric Weighing

A **stoichiometric amount** or **stoichiometric ratio** of a reagent is the optimum amount or ratio where, assuming that the reaction proceeds to completion:

1. all reagent is consumed
2. there is no shortfall of reagent
3. no residues remain

The raw materials are weighed on a digital balance according to the calculated stoichiometry. It is very important to maintain the stoichiometry so that the reaction utilises the maximum starting materials during the solid state reaction. If the stoichiometry is not maintained properly then undesirable changes in the morphology, structure and properties may arise.

3.1.3 Mixing of the Weighed Components

After weighing the chemical precursors in the desired stoichiometric proportion, they are mixed together in a mortar pastel and ground until fine. Then the entire solid powder is transferred into a bottle by addition of acetone and ball milled for 4 to 6 hours. During the mechanical mixing via ball milling the powder is actually ground to fine particles giving more surface area for better reaction.

3.1.4 Calcination

During calcination, the raw materials are heated to any temperature which is below its melting point which leads to a thermal decomposition or phase transition. The volatile precursors get removed during the calcination process. The solid state phase reaction occurs at this stage and with proper temperature crystalline phase formation is achieved. The calcination temperature should be chosen carefully as it alters the density and thereby affecting the electromechanical properties of the final product. The higher the calcination temperature, the better the homogeneity and density of the final ceramic product. Proper calcination at the right temperature gives the best electro- mechanical properties.

3.1.5 Grinding

During solid phase reaction the calcined powder forms lumps and hence in order to smooth these lumps the calcined sample is ground in a mortar pastel.

3.1.6 Binder Addition

After grinding a binder is added to bind the powder into compact paste and dried. Most commonly 3% Poly Vinyl Alcohol (PVA) is used as binder. A very small amount of the binder just enough to soak the powder is used.

3.1.7 Pelletization

After drying out of the binder, it is scraped out from the mortar pastel and ground to fine powder. Then 0.05 gm of the powder is taken and fed into a die set container which is then put into a mechanical pelletizer. Then pressure is applied on the diset and left undisturbed for about three minutes. Finally, the pellet is taken out from the pelletizer.

3.1.8 Binder Burnout

The binder burns out just before the sintering temperature is reached. When the temperature reaches about 500-600^{o}C the polymer binder burns out from the ceramic material leaving behind only the ceramic material.

3.1.9 Sintering

During sintering the temperature is very high for obtaining good densification and microstructure. Microstructure refers to the ceramic morphology at the micro scale such as density, grain size, grain shape, porosity distribution and pore size.The sintering time and temperature should be optimized for obtaining proper densification of the pellets without any abnormal growth. During densification the surface energy is reduced as the free surfaces of the particles disappear. In the case of fine powders, the necessary diffusion length of the atoms for the purpose of sintering becomes shorter. This accelerates the pore diffusion, thus giving rise to high density ceramics. Density of ferroelectric materials increases with sintering temperature. At the sintering temperature accelerated diffusion of the constituent particles take place due to surface energy which promotes crystal bonding at the interface between the two adjacent particles and thus provides sufficient mechanical strengthto the ceramic without significant distortion from the initially moulded shape of the pellet. The sintering temperature of a material is generally two third of its melting temperature. The physical properties of a sintered ceramic does not depend on the property of each fine crystalline particle, but also on the grain boundary and the pores. The sintering of oxide ceramics must be carried out in an oxidizing atmosphere or in air.

3.1.10 Electroding

In this process a metallic layer (usually silver) in paste form is applied on the surface of the intered pellets. The silver paste should adhere very strongly to the ceramic. The silver layer should be practically very thin. Should have zero electrical resistance and must be chemically and electrically durable. These pellets are then heated for some time on a hot plate to form a uniform conducting layer bonded to the ceramic surface. If there is any lack of intimate bonding at the surface of the ceramic with the silver plating the gap between the electrode and the high dielectric constant ceramic acts as a series capacitance of low value.

The product obtained from solid state synthesis route lacks purity and homogeneity. One of the major drawbacks is the requirement of very high calcination and sintering temperatures which leads to more power consumption. Considering these factors the chemical route for synthesis is adopted due to lower calcinination and sintering temperatures and ensuring homogeneity due to chemical reactivity in solution state which favours forward reaction of chemical precursors.

3.2 Chemical Route

This route is adopted for synthesis of ceramics as it leads to homogeneous powder and such ceramics have low temperature requirements for calcination and sintering leading to final phase formation. Also the particles are finer in this route than in solid state route. These ceramics have better surface to volume ratio and hence they have increased reactivity. It is based on the phase transition of a sol obtained from metal alkoxides or organometallic precursors. One major advantage of this process is that the composition can be controlled perfectly. Densification is achieved at a much lower temperature. Ceramics prepared through this route find applications in optics, electronics, energy, space , biosensors, medicine (eg: controlled drug release) and separation chromatography.

3.2.1 Raw Materials used

The starting materials chosen for preparation of $Bi_{3.25}La_{0.75}Ti_3O_{12}$ by chemical route are Bismuth Nitrate ($Bi(NO_3)_{2.}5H_2O$), Lanthanum Nitrate ($La(NO_3)_3.6H_2O$) and Titanium Butoxide Polymer ($Ti(OCH_2CH_2CH_2CH_3)_4$).

3.2.2 Stoichiometric Weighing

The starting materials are weighed on a digital balance according to their calculated stoichiometry. The stoichiometry is calculated from the molecular weight of the precursor divided by the number of atoms present in the compound molecule and then multiplied by the required number of atoms for the doped system.

3.2.3 Solution preparation

The weighed constituents are dissolved in acetic acid (CH_3COOH) individually and stirred with the help of a magnetic stirrer on a hot plate to allow for the reaction to occur as heat increases the rate of reaction in the forward direction. This is done until the solutions come clear.

3.2.4 Mixing

The individual solutions of the two inorganic precursors(Bismuth Nitrate and Lanthanum Nitrate) are mixed together and a clear mixed solution is formed. Finally with continuous stirring and heat at about 60 the polymer precursor (Titanium Butoxide) is added by weighing it in a beaker. A white precipitate forms.

3.2.5 Drying

The precipitate formed on mixing is dried on a hot plate until only a gel kind dry material is formed. The gel is again dissolved in a little acetone and dried to obtain powder. T he powder thus obtained is ground to get fine powder then it is calcined at 600^0C just as in solid state method followed by pelletization and sintering at 1150^0C. The sample obtained by this route has better properties than those obtained by conventional solid state method and also chemical route

prepared samples have lower calcination temperature because phase formation of sample prepared by the chemical route takes place at a lower temperature which is one of its major advantage as it saves power.

Chapter 4: Characterization Methods

4.1 Density Measurement

Density measurement is based on the famous principle called Archimedes principle. This principle states that any object wholly or partially immersed in water experiences a buoyant force equal to the weight of the water displaced by the object, with the justification for a sunken object that volume of the displace fluid equals the volume of the object. The formula that is presently in use in the field of material science is a modification of the Archimedes principle.

$$Density = \frac{D}{S - W} \times Density\ of\ kerosene$$

Where, D = dry weight

S = soaked weight

W = suspended weight

Density of kerosene =0.81g/cc

Immersing the bulk ceramic in kerosene fills up the porous spaces and releases the air in it which can contribute to error in density measurement. Unwanted pores make the ceramic brittle and also affect properties of the sample such as dielectric measurement and hysteresis loop measurments thus these are removed by immersing the pellets in kerosene.

4.2 X-ray Diffraction

This characterization technique is employed for phase identification of a crystalline material and gives some idea of unit cell dimensions. It helps to determine the crystal structure. The material to be analysed should be in finely ground powder form or in the form of a homogeneous pellet.

4.2.1 Fundamental Principle

Max Von Laue, in 1912, discovered that crystal planes act as diffraction gratings when X-Ray is passed through them. The crystal planes diffract the monochromatic X-rays. X-Rays also give valuable information like the atomic spacing of planes in a crystal lattice. Fundamental principle involved in X-Ray diffraction is the constructive interference of monochromatic X-Rays and a crystalline sample. Generation of X-Rays takes place in a cathode ray tube. These rays are then filtered to produce monochromatic X-Rays.

Further these monochromatic X-Rays are collimated and finally aimed towards the sample. The constructive interference of the X-Rays and the crystalline material takes place only when the phase difference is an integral multiple of the wavelength. In other words, it should satisfy Bragg's Diffraction condition ($2d\sin\theta = n\lambda$).

4.3 Scanning Electron Microscopy

A Scanning Electron Microscope scans a particular sample in a raster scan pattern. The high energy electrons from the electron beam interact with the surface of the sample and pass on valuable information such as surface morphology, grain size and grain boundary by producing signals. These signals are a result of the interaction of the electrons with the atoms of the sample at or near the surface. Magnification is possible on a wide scale ranging from 10 to about 5×10^6 times.

4.3.1 Fundamental Principle

An electron beam having energy in the range from 0.2 to 40 keV is focussed to a spot with the help of two condenser lenses. The spot dimensions are of the order of 0.4 to 5 nm in diameter.. The beam then passes through pairs of deflector plates which deflect the beam in the direction of X and Y axes respectively. This leads to scanning in a raster fashion over some rectangular area of the surface of the sample. During the interaction of the primary electron beam with the sample, there is energy loss due to repeated random scattering and scattering within a small volume of the specimen termed as interaction volume. The dimensions of this volume ranges from 100nm to about 5µm inside the volume. The exchange of energy between the electron beam and the sample leads to reflection of high energy electrons as a result of elastic scattering. This energy interchange also results in emission of secondary electrons due to inelastic scattering. Electromagnetic radiations are also emitted due to this exchange interaction. Each of these can be detected by detectors specialised for this purpose. The current absorbed by the specimen sample can also be detected and used to create image of current distribution in a particular sample. Amplifiers are used for amplifying the information signals which are displayed on a computer screen. The display is synchronised with the beam of the sample in the microscope. Therefore the final image that is obtained is a distribution map of the emitted signal intensity from the area that has been scanned of that particular sample. The image can be captured digitally with a screenshot and saved to a computers hard disk which is later analysed to obtain grain size.

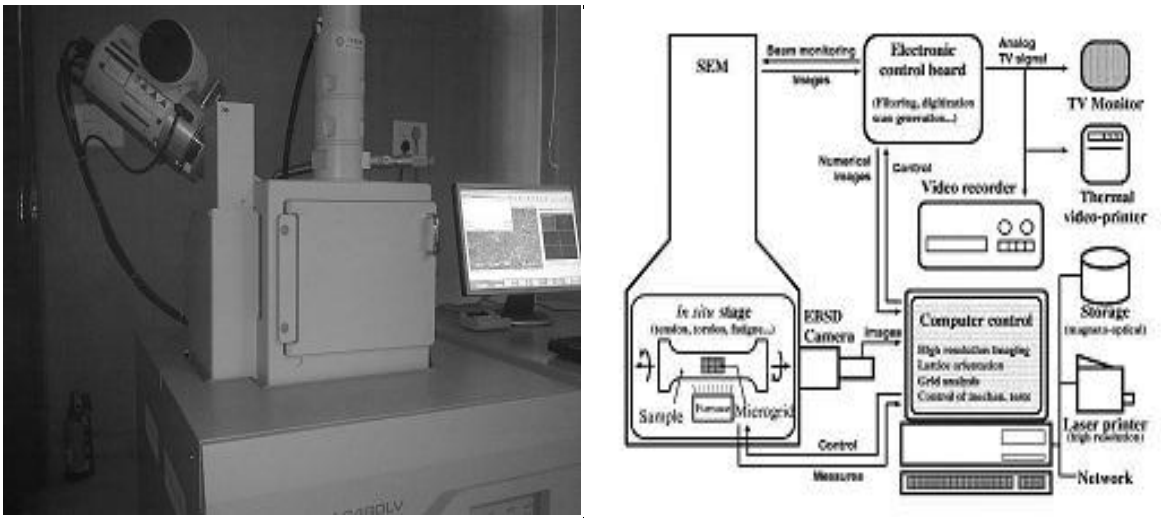


Fig 6: Scanning electron microscope outside and inside view

4.4 Dielectric Study

Dielectric constants of ferroelectric materials range from several hundred to several thousands. For studying the variation of dielectric constant with temperature at particular frequencies, the LCR meter is run which measures the variation of capacitance with temperature and from the data obtained the dielectric constant is calculated and plotted versus temperature in Origin Software. The LCR meter is an electronic equipment used to measure inductance, capacitance and resistance of a dielectric sample. These are usually determined from the impedance of a sample. The device is subjected to an a.c. voltage. The meter detects the voltage and current through the device and subsequently the impedance. The observations were collected from a computer interfaced HIOKI 3532-50 LCR-HITESTER.

Fig 7: HIOKI 3532-50 LCR-HITESTER for dielectric measurement

4.5 Electric Field vs. Polarization Measurement

This measurement was done with the help of a conventional sawyer-tower circuit. The electric field is increased by signalling the voltage through the signal generator. The direction of the voltage is reversed at high frequency, and the voltage is measured across the reference capacitor. The sample and the capacitor are kept in series with one another and therefore have the same charge. The polarization is plotted in the oscillating field by representing the voltage applied in the X-axis and the surface charge on the Y-axis. Capacitance of the reference capacitor is kept higher than the ferroelectric sample so most of the voltage thus is accommodated in the ferroelectric sample itself.

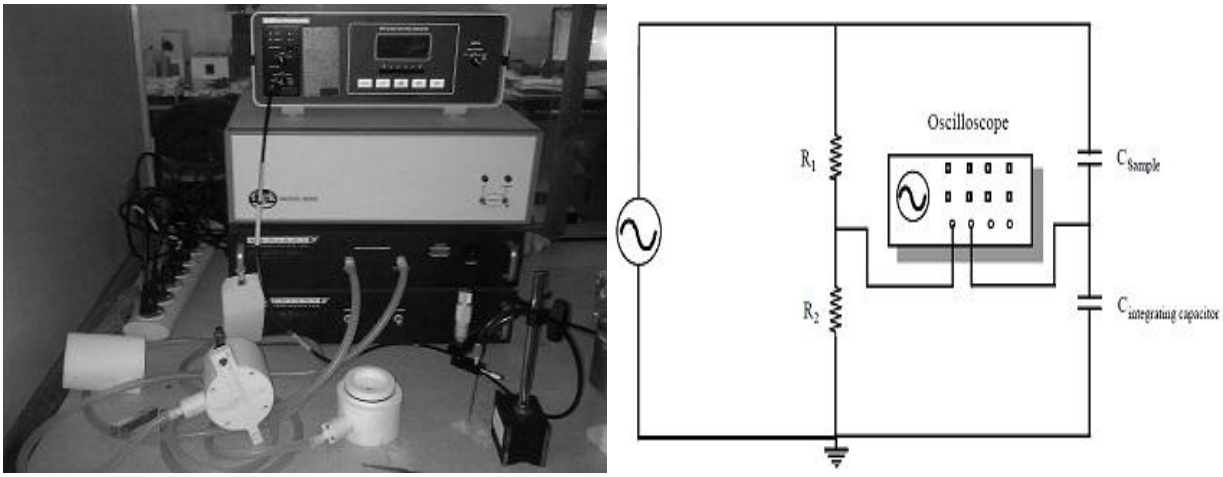


Fig 8: Experimental set up(left) and Sawyer Tower circuit [5](right) for p-e loop measurement

Chapter 5:Results and Discussion

5.1 Density

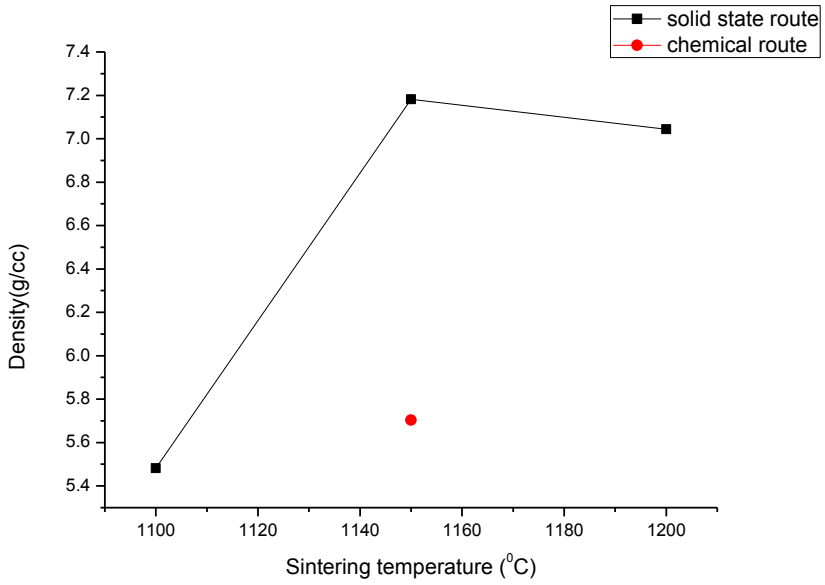


Fig9:Density plot of solid state route sample and chemical route sample

The plot of temperature versus density of the samples obtained by solid state route show an increase from 1100^0C to 1150^0C and again decreases from 1150^0C to 1200^0C. From this plot it is realised that best density occurs at 1150^0C. Therefore the sintering of the sample obtained by chemical route is done at 1150^0C. Even though from literature it is found out that density of chemical route samples out to be greater than that of solid state route experimentally it was not found so.

Preparation route	Temperature(in ^{0}C)	Density (in g/cc)
Solid state	1150	7.1820
Chemical	1150	5.7029

5.2 X-Ray Diffraction

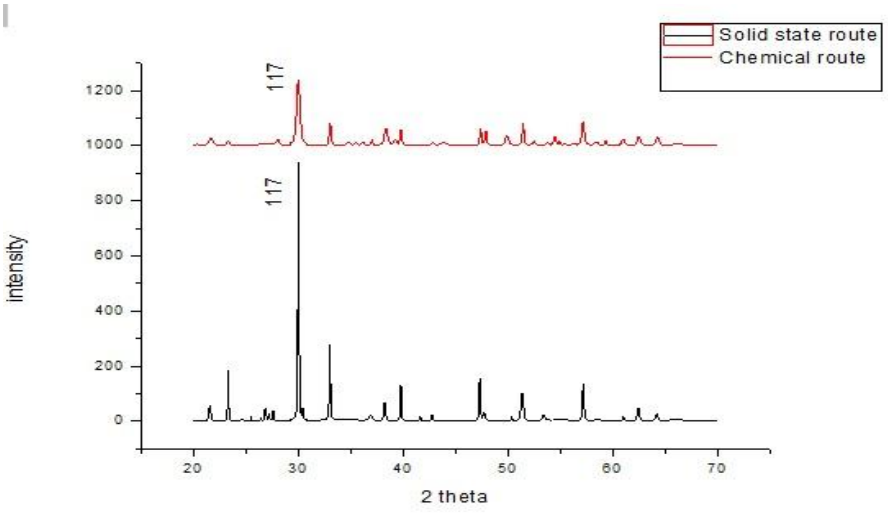
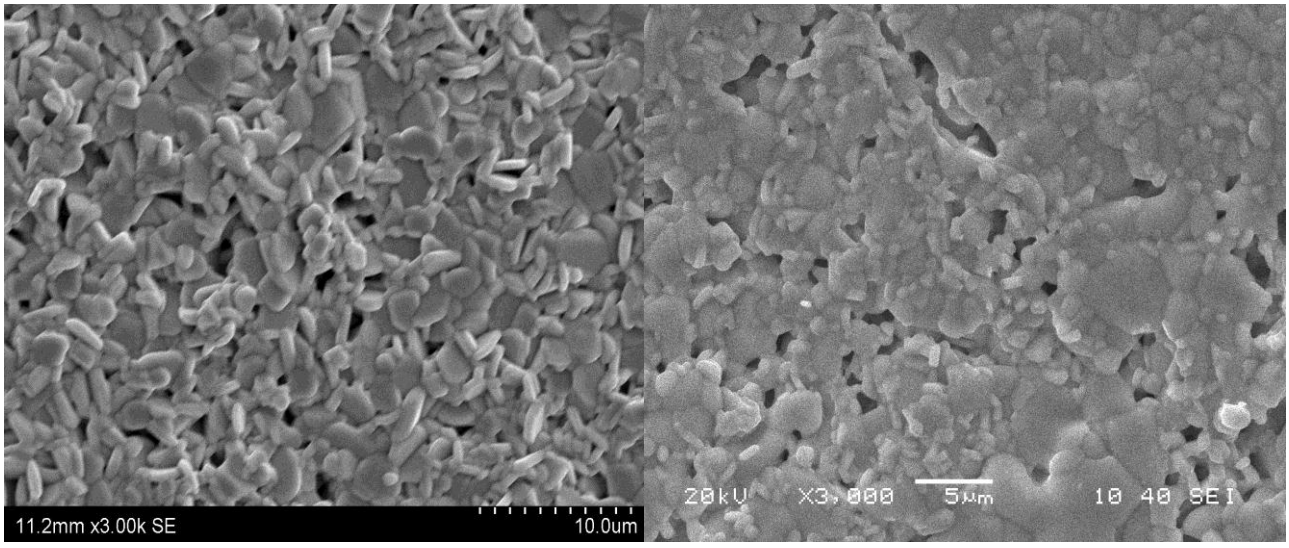


Fig 10: Diffraction peaks of solid state sintered sample and chemically sintered sample

The X-Ray diffraction pattern confirms the layered perovskite structure. Phase formation was achieved in BLT conventional route at 750^0C and in BLT chemical route at 600^0C. XRD patterns clearly indicate orthorhombic structure from the reference pattern number 73-2181 for samples prepared by both solid state route as well as for samples prepared by the chemical route. The unit cell structure was found to be orthorhombic in accordance with matched reference pattern. Earlier a phase transition from orthorhombic to tetragonal unit cell structure was reported with 25% La doping[8,9] however in our case no such changes in structure are observed .The lattice parameters in accordance with the data have been summarized in Table below.

Sythesis process	Structure	a(Å)	b(Å)	c(Å)
Solid State	Orthorhombic	5.4100	5.4480	32.8400
Chemical Route	Orthorhombic	5.4480	5.4110	32.8300

5.3 SEM Characterization Study



JPEG images obtained by scanning are used to find the grain sizes. The grain sizes are more uniform in the chemical route synthesised samples than in the conventionally synthesised samples.

Fig 11: SEM micrographs of BLT solid state (left) and chemically sintered pellets (right).

From SEM micrographs study the grain size of the sample prepared by conventional route sintered at 1150^0C was found to be 1.8µm and that of the sample prepared by chemical route and sintered at 1150^0c was found to be 1.4µm.

5.4 Dielectric Measurements

From the data collected from the set up the dielectric constant versus temperature plot and the tangent loss versus temperature plot was obtained.

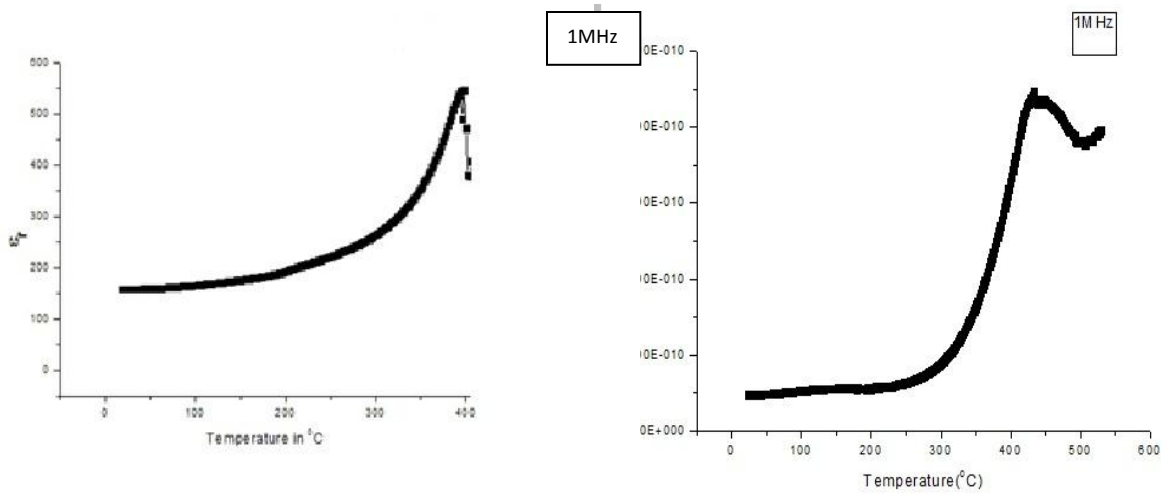


Fig 12: Variation of dielectric constant with temperature in solid state sintered sample (left) and chemically sintered sample (right)

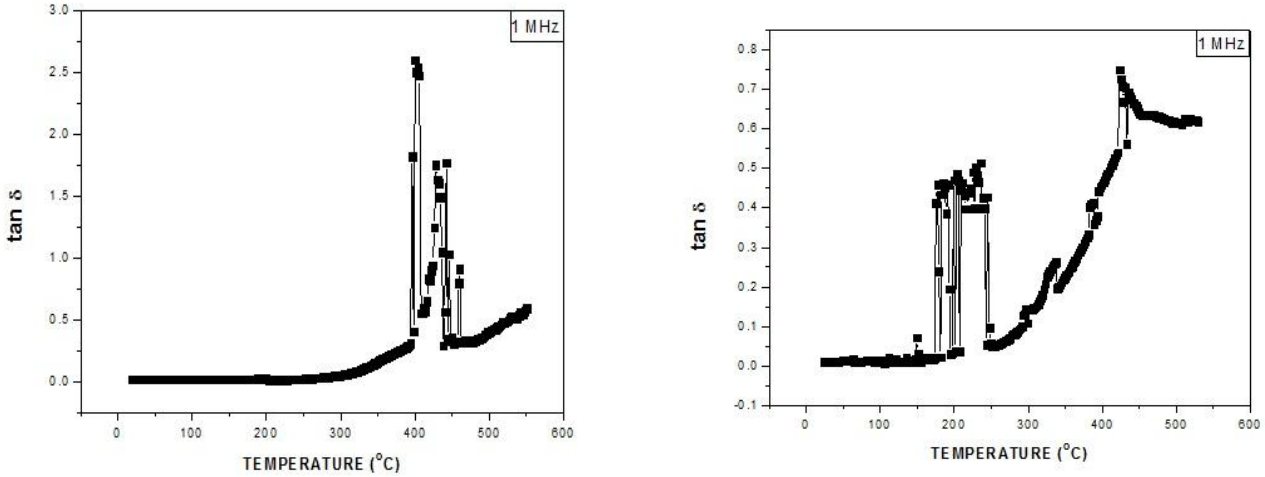


Fig 13: Dielectric losses in BLT solid state sample (left) and BLT chemical route sample(right)

From figure 12 it can be seen that the dielectric constant is increasing with time at a constant frequency of 1 MHz. From the graph it is observed that the T_c is higher than 400^0Ctemperature and since the limitation of the instrument is that it can achieve temperature only upto 550^0C therefore we are unable to determine T_c from the dielectric measurement. . The dielectric loss curve however shows a slight

increase and then random fluctuations in both the solid state synthesised sample and chemically synthesised sample which make it difficult to interpret. Since it is increased slightly therefore we can say that loss occurs and hence the sample is not fit for electronic applications. From literature the T_c was found to be around 630^0C.Thus our success can be accounted only for increase of dielectric constant.

5.5 P-E Loop Analysis

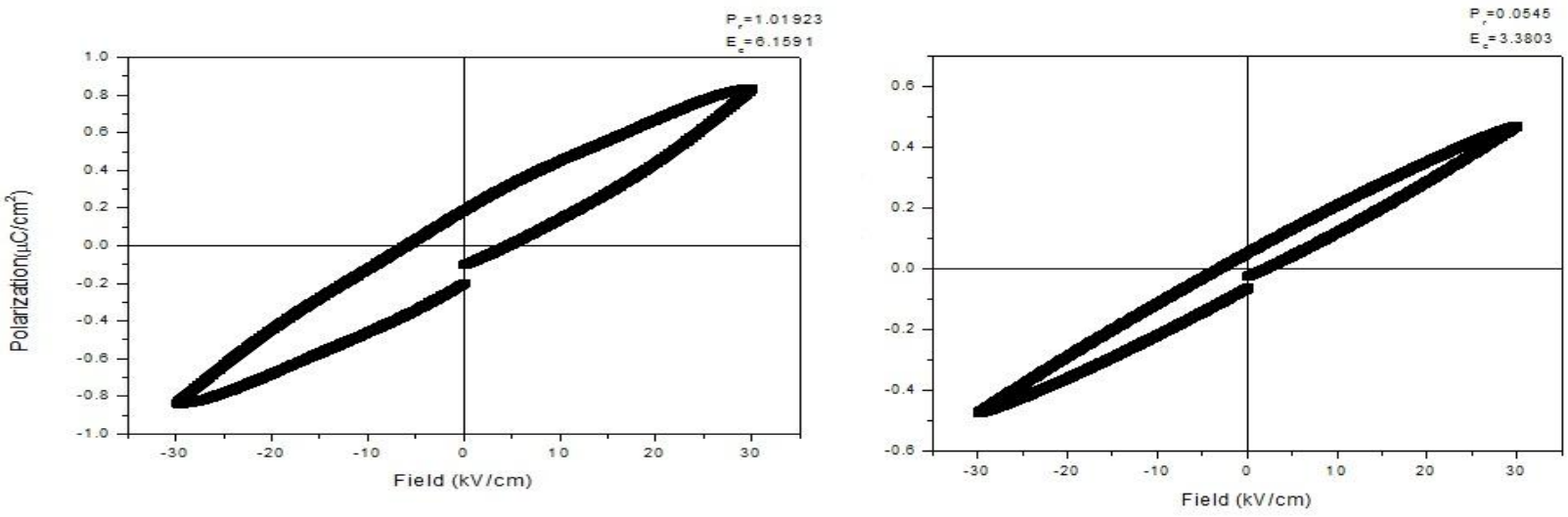


Fig 14: Hysteresis loop of solid state sample of 1150^0C sintered sample at 30 kV applied field(left) and chemically prepared sample of 1150^0C sintered sample at 30kV applied field(right)

The polarization versus Electric field curve did not yield better properties as would have been desired. Some contribution to the non comparable properties has also been made by the instrument which would not allow the loop to close. However, the comparison of the P-E loops of BLT conventional and BLT chemical route have been presented below.

From the P-E loops the remnant polarization and coercive field values are found and it is observed that for same 30 kV field the remnant polarization value is better for the solid state route as high P_r value is desirable for application of BLT sample and the coercive field is better for the chemical route prepared sample as low E_c value is desirable. The retention failure of BLT sample is a reason why its low fatigue nature cannot be utilized.

Chapter 6: Conclusions

From the density measurement we have observed better density of solid state synthesized BLT however from literature it was seen that better density is obtained from BLT samples synthesised by chemical route. XRD pattern shows orthorhombic structure which is the structure in accordance with Literature Survey. From SEM micrographs better homogeneity of chemically synthesised BLT was evident and the grain sizes were also smaller than solid state synthesized sample. Dielectric measurements have shown T_c is at higher temperature than could be achieved. Appreciable loss has occurred in both forms of BLT samples. P-E loop measurements have shown high remnant polarization in solid state route and low coercivity in chemically synthesised sample.

Chapter 7: Future work

$Bi_{3.25}La_{0.75}Ti_3O_{12}$ is a widely studied composition. In future I would like to take up work that may include synthesis and characterizations of other composition of Bismuth Lanthanum Titanate and main focus would be on how to achieve better ferroelectric properties such as high remnant polarization, low coercivity which will pave the way for use of BLT ceramics in electronic applications. Also, I would like to prepare thin films based on different BLT compositions and correlate their properties with bulk BLT ceramics.

Chapter 8: References:

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